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Introduction of Sulfur Into Copper Converter Slags To Produce Copper Matte

By J. I. Paige and W. E. Anable

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
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INTRODUCTION OF SULFUR INTO COPPER CONVERTER SLAGS TO PRODUCE COPPER MATTE

By J. I. Paige[1] and W. E. Anable[1]

ABSTRACT

As part of a continuing effort to develop technology that maximizes mineral and metal recovery from domestic resources, the Bureau of Mines investigated a method to totally utilize copper converter slags without recycling them back through the matte smelting furnace. The research was directed toward (1) recovering the contained copper in converting slags by producing a recyclable copper-iron matte, (2) carbothermically reducing the slags to recover the iron, and (3) producing slag wool from the depleted slags.

This report deals with the reduction of three industrial converting slags, containing 2.0 to 7.3 wt-pct Cu, in an 800-kVA electric arc furnace to produce a recyclable copper-iron matte.

The addition of sufficient iron pyrite to provide 29 to 113 pct of the stoichiometric sulfur (based on producing 40-pct-Cu matte) produced a recyclable matte (36 to 61 pct Cu) at an energy consumption of 520 to 700 kWh per ton of solid material charged. The expected energy saving for treating molten slag in an electric furnace (5- to 9-MVA range) is about 400 kWh per ton of molten slag treated.

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INTRODUCTION

Copper is critical to the industrial base of the United States and the free world. And as the grade of ore being mined decreases, the technology for extracting this vital metal must be modified and improved. The main route of copper losses from smelters is in the discarded slags, which account for 1 to 2 pct of the total copper produced by the smelter. This is equivalent to a smelter efficiency of 98 to 99 pct; this is very high, but copper is a valuable product and any loss contributes substantially to smelting costs. For example, the cost of losing 20 lb Cu at $0.90/lb is $18. This is a significant fraction of the direct cost for smelting 1 ton of copper from concentrate ($235).

The extraction of copper consists of the following four steps: (1) concentration by froth flotation, (2) roasting, (3) matte smelting, and (4) converting to blister copper. Slags are produced during the matte smelting and converting stages of the process. The smelting furnace slags contain 0.2 to 1 wt-pct Cu and are discarded directly. However, the converter slags contain 2 to 15 wt-pct Cu and are too valuable to discard. Consequently, every copper smelter is faced with the problem of recycling converter slag to the smelting furnace. Solutions range from returning the molten slag directly to the smelting furnace, to slow cooling the slag, followed by crushing, grinding, and flotation to recover the copper.

Although the practice of recycling molten converter slags alone recovers the bulk of the copper contained in the slag, there are a number of undesirable effects on smelting furnace operations.[2] Among these are (1) introduction of magnetite into the smelting furnace, resulting in a layer of suspended magnetite concentrated at the slag-matte interface; (2) lowering the capacity of the furnace to smelt copper concentrate; and (3) additional flux burden, which also lowers furnace capacity and increases the cost of flux per unit of copper smelted.

The process investigated was based on treating already molten converter slags in a separate electric furnace to (1) produce a copper-iron matte suitable for recycle to the converter, (2) carbothermically reduce the slags to recover the iron, and (3) produce slag wool from the depleted slags, which are principally composed of silicates of calcium, magnesium, and aluminum. This report deals with the reduction of converter slags containing 2.0 to 7.3 wt-pct Cu in laboratory-scale (50-lb) and engineering (1-ton) batch furnaces.

The carbothermic reduction of slags to recover the iron has been investigated previously by Paulson and Hunter.[3] A preliminary evaluation of the glass fiberization potential of the depleted slags was done at the Bureau of Mines' Tuscaloosa Research Center, and good fibers were obtained from each of the three slags. The research program was terminated following the preliminary investigation.

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[2]Itakura, K., T. Nagano, and J. Sasakura. Converter Slag Flotation--Its Effect on Copper Reverberatory Smelting Process. J. Metals, v. 21, July 1969, pp. 30-34.

Oudiz, J. J. Control of Oxidizing Conditions in Copper Smelting. J. Metals, v. 25, May 1973, pp. 22-25.

[3]Paulson, D. L., and W. L. Hunter. Recovering Iron From Copper Smelting Furnace Slags by Carbon Injection. BuMines RI 8211, 1977, 14 pp.

MATERIALS

The three converter slags used in the investigation were obtained from commercial copper smelters. Each of the slags were dried, crushed to minus 1 inch, blended, and sampled. Chemical compositions of the slags and furnace additions used during this investigation are shown in table 1. Electron microprobe analyses were conducted on the complex converter slags to identify the various phases present. Two noncrystalline phases were present which were found to be iron silicates with variable composition containing Fe, Si, Pb, Cu, Sb, and Zn as well as other minor elements. Much of the fayalite crystallized as lath or needles, and the magnetite crystallized as dendrite and rounded particles within the glassy phases. Copper sulfides (bornite, chalcocite, and chalcopyrite) and copper metal were the primary sources of copper in the slags.

TABLE 1. - Chemical analyses of slags and furnace additions, wt-pct

	Cu	Fe+[1]	S	Pb	Zn	As	Ni
Slag A.....	7.34	40.6	2.03	4.66	1.64	0.34	0.28
Slag B.....	4.35	39.3	1.08	1.68	7.69	.04	.10
Slag C.....	2.02	44.8	2.23	.02	.32	.01	.03
Quartz.....	NA	1.30	NA	.16	NA	NA	NA
Pebble lime	NA	.07	NA	NA	NA	NA	NA
Pyrite.....	NA	40.7	50.4	NA	NA	NA	NA
Coke breeze	NA	NA	.73	NA	NA	NA	NA
Utah coal..	NA	NA	.73	NA	NA	NA	NA

	Mo	C	CaO	MgO	Al_2O_3	SiO_2	Fe_3O_4[2]
Slag A.....	NA	NA	0.75	0.55	1.18	25.7	25.9
Slag B.....	NA	NA	1.26	.12	1.52	25.5	18.4
Slag C.....	0.10	NA	.35	3.94	3.03	27.3	45.4
Quartz.....	NA	NA	NA	NA	.23	97.3	NA
Pebble lime	NA	NA	96.1	.46	.15	2.94	NA
Pyrite.....	NA	NA	NA	NA	NA	5.48	NA
Coke breeze	NA	88.9	.26	.09	2.55	5.52	NA
Utah coal..	NA	48.9	.37	.07	1.59	3.15	NA

NA Not analyzed.

[1]Total iron units, ferric + ferrous + metallic.

[2]Calculated, assuming all ferric iron is in the form of magnetite.

Following is a list of the major phases identified by electron microprobe analyses and their approximate order of prevalence.

Phase:	Approximate amount present, pct
Fayalite.....	25-40
Magnetite.....	15-30
Noncrystalline.....	15-30
Cu sulfide.....	1-3
Fe metal.....	1-3
Cu metal.....	1-3

ELECTRIC FURNACE TESTS ON COPPER CONVERTER SLAGS

Laboratory-scale tests were made in a 50-kVA electric furnace using approximately 50-lb batches of copper converter slag. The engineering tests were made in an 800-kVA electric arc furnace using approximately 2,000-lb batches of copper converter slag.

All calculations of sulfur requirements for stoichiometric conversion of copper compounds in the slag to Cu_2S in the matte were based on forming a matte containing 40 wt-pct Cu and 28 wt-pct S. Sulfur reductant was added as pyrite (FeS_2). The sulfur present in the converter slag (1 to 2 wt-pct) was ignored in the computation because the sulfur content of the slag remained nearly constant during matte formation. For example, in table 1, 50 lb of slag A containing 7.34 wt-pct Cu would require 2.6 lb S or 5.1 lb of pyrite.

Converter slags typically contain 25 to 50 wt-pct magnetite (Fe_3O_4), which requires reduction to FeO during sulfurizing tests. Hence, for purposes of calculating carbon requirements, it was assumed that one mole of carbon was required for each mole of magnetite in the slag. For example, a slag containing 25.9 wt-pct Fe_3O_4 (slag A in table 1) required 0.67 lb C or 1.4 lb of Utah coal per 50 lb of slag at stoichiometric reduction of ferric oxide to the ferrous state.

Copper in converter slags is present as oxide, sulfate, or ferrite (CuO, $CuSO_4$, $CuO \cdot CuSO_4$, $CuO \cdot Fe_2O_3$) in addition to entrained metal. The copper oxide also requires reductant, but the uncertainty in the proportion of each oxidized species introduces considerable uncertainty in the calculation of reductant requirements. A reasonable assumption is that most of the copper is present as CuO, thereby requiring one mole of carbon for each mole of copper in the slag. Slag A in table 1 (7.34 wt-pct Cu) would require 0.70 lb C or 1.4 lb of Utah coal per 50 lb of slag. Total carbon requirement, assuming the formation of CO, is then the sum of the requirements for oxidized iron and copper or about 2.8 lb of Utah coal per 50 lb of slag.

Equipment and Procedures for Laboratory-Scale Tests

The 50-kVA (size W) electric arc furnace used for the preliminary tests is shown in figure 1. Single-phase current for the furnace was supplied by a 50-kVA welding transformer that was operated from a portable control panel near the furnace. Manually operated rack-and-pinion-mounted electrode clamps controlled the position of the 2-in-diam graphite electrodes. The furnace shell, approximately 17 in high, was lined with a high-MgO ram-cast mix, which resulted in a working crucible of 12-in ID. The furnace shell was covered with a cast high-alumina roof that was supported by a water-cooled ring. A taphole was provided at hearth level to remove the molten products. Furnace offgases were evacuated by a 7,500-cfm fan, which exhausted into a positive-pressure cyclone and baghouse to collect entrained dust.

During a test, the blended charge (slag, quartz, lime, pyrite, and coal) was fed to the furnace with a 4-in, variable-speed belt feeder. The feed rate was varied as necessary to maintain an even melting rate with very little buildup of feed on top of the bath at a power input of about 40 kW. Upon completion of feeding, the power input was reduced to about 20 kW and the furnace was held at temperature (1,150° to 1,400° C) for 20 min to allow for separation of the heavier copper-iron matte and the slag. The products were then tapped out of the furnace, cooled, and sampled for analysis by wet chemical techniques.

Results of Laboratory-Scale Tests

The first series of laboratory tests was designed to determine coal and silica requirements for subsequent larger

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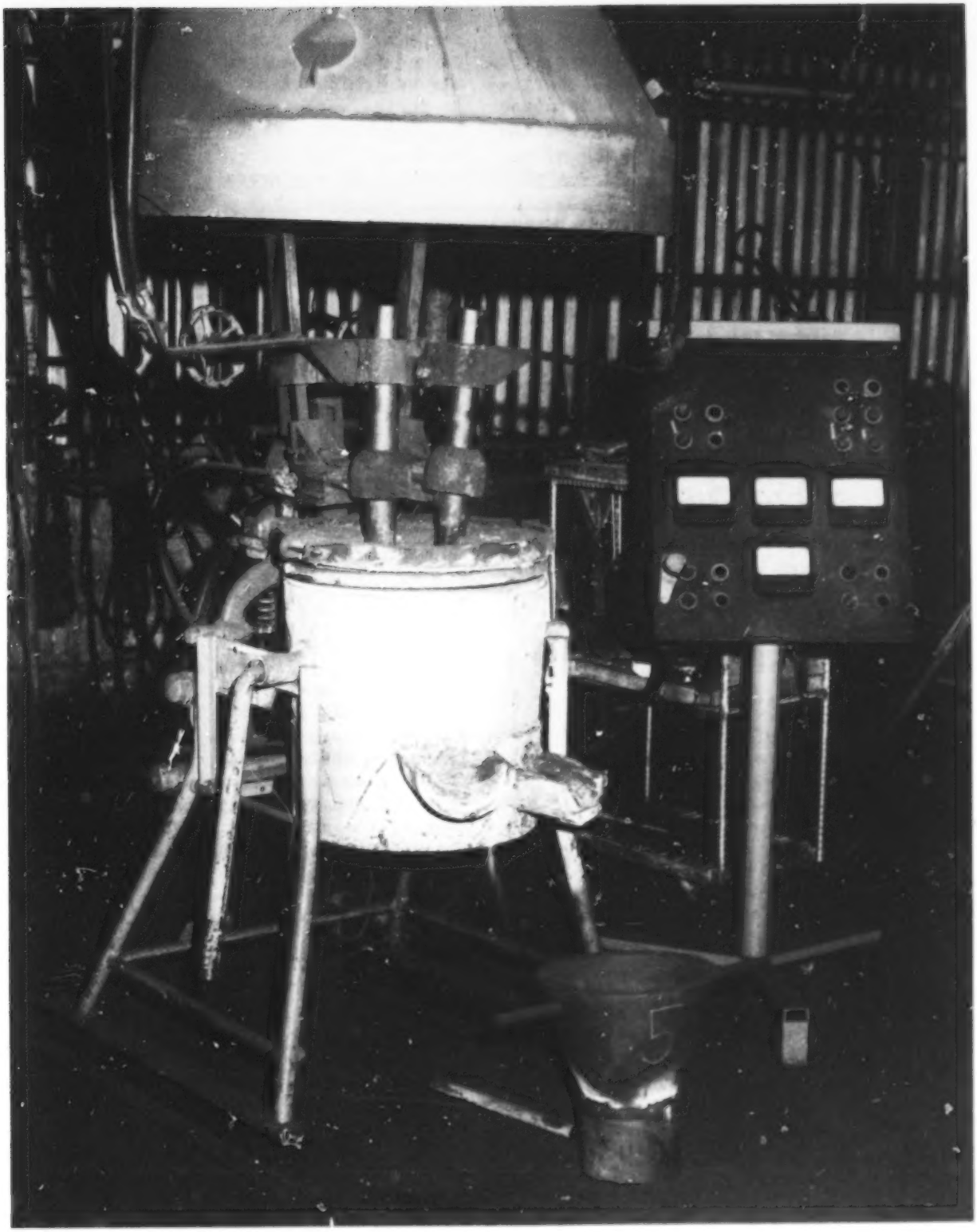

FIGURE 1. - The 50-kVA electric arc furnace.

scale tests. The results (table 2) are plotted in figure 2 in terms of copper recovery versus quartz additions for three levels of coal in the charge. Quartz additions were made to increase the level of silica in the slag to the range of typical reverberatory furnace slags (35 to 40 pct), and coal additions ranged from about 40 pct to 120 pct of the stoichiometric requirement (2.8 lb), as defined previously.

TABLE 2. - Effect of carbon reductant, laboratory-scale tests

Test	Charge,[1] lb		Analyses, wt-pct						Recovery, pct Cu
	Coal	Quartz	Matte			Slag			
			Cu	Fe	S	Cu	Fe	SiO_2	
1..	1.1	0	40.6	22.2	23.0	1.30	37.4	25.2	83
2..	1.1	2.6	38.6	22.1	23.3	.79	39.2	31.7	73
3..	1.1	3.8	38.8	21.4	23.5	1.00	40.4	29.0	67
4..	1.1	4.6	34.5	24.9	23.3	.60	37.2	32.0	55
5..	2.2	0	34.3	29.4	23.5	1.00	43.8	28.7	86
6..	2.2	2.6	33.9	29.5	21.3	.70	35.8	28.9	84
7..	2.2	3.8	34.8	28.5	22.3	.82	42.0	35.5	86
8..	2.2	4.6	34.5	32.5	22.0	.76	38.5	33.7	70
9..	3.3	0	33.2	32.4	19.2	1.00	40.6	30.2	87
10..	3.3	2.6	34.2	32.8	18.8	.88	39.7	33.7	93
11..	3.3	3.8	35.7	34.0	18.4	.75	38.4	36.2	95
12..	3.3	4.6	37.7	33.7	21.0	.71	38.4	41.9	105

[1]Each test charge contained 50 lb slag A (table 1) and 6.6 lb pyrite.

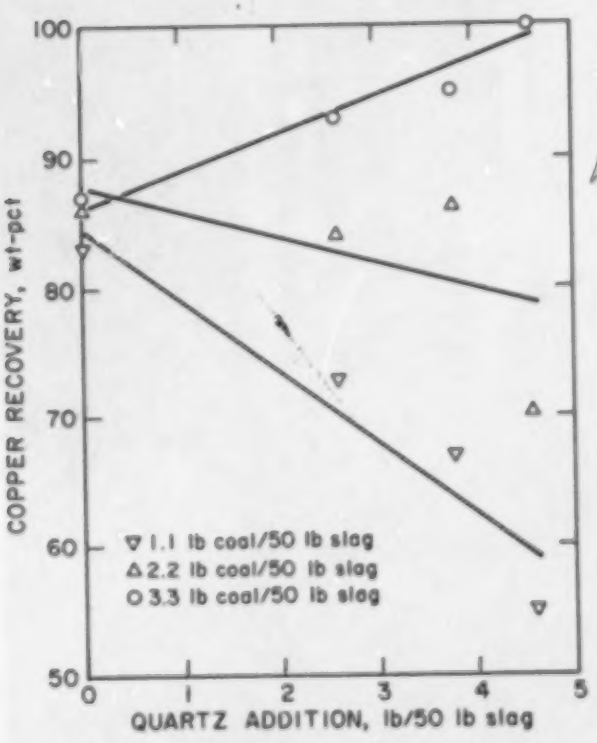

FIGURE 2. - Effect of coal and silica on copper recovery, laboratory-scale tests.

Because of the inherent mixing caused by the electric arcs, the copper-iron matte does not settle out completely in a small furnace like the size W. Nevertheless, the data are useful and indicate that copper recovery in the matte phase increased as the silica content of the slag approached saturation only if the amount of reductant exceeded the stoichiometric requirement.

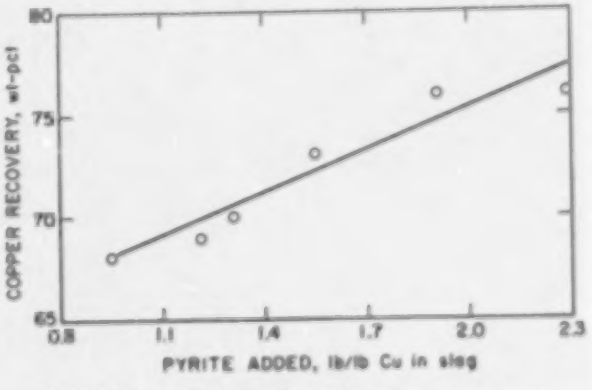

FIGURE 3. - Effect of pyrite on copper recovery, laboratory-scale tests.

A second test series was designed to study the effect of sulfur reductant on copper recovery from the converter slag. Iron pyrite was added to increase the amount of sulfur present from 69 to 165 pct of stoichiometric (2.6 lb), and quartz was added (5.5 lb per test) to bring the silica content of the slag up to about 35 pct. The data from the first series did not justify using a higher silica content in the slag, but common smelting practice is to maintain the silica content of the slag at or near saturation (35 to 40 pct) to insure optimum matte-slag separation. Data (table 3) plotted in figure 3 show that copper recovery increased from 68 pct up to 76 pct as the pyrite in the charge was increased from 0.9 to 2.3 lb per pound of copper in the slag. The data points indicated that the copper recovery was maximum at about 2.0 to 2.3 lb of pyrite per pound of copper in the slag, but in view of the normal scatter in data obtained with the size W furnace, the data were fitted to a linear regression analysis shown by the curve in figure 3. At the highest recovery level, the slag was at silica saturation and was approaching the normal ratio of iron to silica (1:1) found in reverberatory furnace slags.

TABLE 3. - Effect of sulfur reductant, laboratory-scale tests

Test	Charge,[1] lb		Analyses, wt-pct						Recovery, wt-pct
			Matte			Slag			
	Pyrite	Coal	Cu	Fe	S	Cu	Fe	SiO_2	Cu
13..	3.5	1.6	48.3	14.1	20.2	1.00	36.9	33.0	68
14..	4.4	1.6	42.5	16.7	21.0	1.00	33.3	32.3	69
15..	4.8	1.6	41.1	20.6	22.9	.76	39.3	33.3	70
16..	5.7	1.6	39.4	23.7	23.3	1.20	37.4	30.5	73
17..	7.0	1.6	39.8	26.8	21.4	1.43	39.5	36.6	76
18..	8.4	1.6	39.6	32.1	25.1	1.52	38.6	36.6	76

[1]Each test charge contained 50 lb slag A (table 1) and 5.5 lb quartz.

Fluxing tests were made to evaluate the effect of increasing the weight ratio of CaO to Al_2O_3 in the slag and on the efficiency of isolating the copper into the matte phase. Additions of these oxides tend to stabilize the slag structure[4] and are generally considered beneficial in small amounts (<10 pct). Tests were made at two levels of alumina (1.1 and 2.2 lb per charge), and lime additions were made to increase the ratio of CaO to Al_2O_3 from 0.6 up to 4 in as-received slag.

Data (table 4) plotted in figure 4 show that copper recovery progressively decreased as the weight ratio of $CaO:Al_2O_3$ in the slag increased. Copper recovery decreased from 84 to 64 pct in the first series and from 58 to 39 pct in the second series. The exact reason for the decrease in copper recovery was not determined. Although the lime-alumina additions offered only minor changes in viscosity and liquidus temperature over the range examined, and refractory erosion was minimal during each of the tests, the small additions of lime and alumina were detrimental to isolating the copper into the matte phase.

[4]Biswas, A. K., and W. G. Davenport. Extractive Metallurgy of Copper, ed. by D. W. Hopkins. International series on materials science and technology, Pergamon Press Ltd., Oxford, England, v. 20, 1st ed., 1976, p. 94.

TABLE 4. - Effect of flux additions, laboratory-scale tests

Test	Furnace charge,[1] lb		Ratio, CaO/Al_2O_3	Analyses, wt-pct						Recovery, wt-pct
				Matte			Slag			
	Lime	Alumina		Cu	Fe	S	Cu	Fe	SiO_2	Cu
19....	1.3	1.1	1:1	41.1	22.3	19.6	0.92	37.0	36.4	84
20....	3.1	1.1	2:1	34.7	28.7	19.5	1.00	34.3	31.7	71
21....	4.6	1.1	3:1	33.2	27.4	16.8	1.00	34.7	34.8	64
22....	6.4	1.1	4:1	35.3	26.2	19.0	1.10	33.7	33.0	67
23....	2.2	2.2	1:1	31.5	29.1	22.4	.86	34.1	32.7	58
24....	5.3	2.2	2:1	29.7	29.3	19.7	1.41	32.7	30.7	53
25....	7.7	2.2	3:1	27.1	33.6	21.6	.84	30.0	29.4	46
26....	10.6	2.2	4:1	21.9	37.2	21.9	.91	28.7	29.5	39

[1]Each test charge contained 50 lb slag A (table 1), 6.6 lb pyrite, 2.2 lb coal, and 5.5 lb quartz.

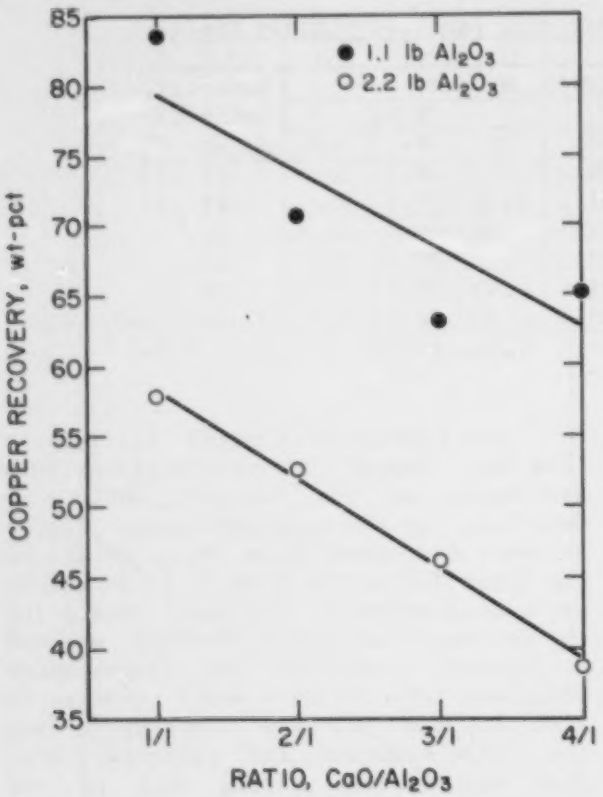

FIGURE 4. - Effect of lime and alumina on copper recovery, laboratory-scale tests.

Some of the impurities (Zn, Pb, Bi, Sn, Sb, As) contained in the converter slag escaped the melting furnace as dust and as vapor during the sulfurizing tests. Samples of the dust were collected by a sampling device fitted with a filter paper and a suction system. Analyses of samples collected from typical runs are shown in table 5. The relative concentration of impurities in the fume was calculated according to Keller[5] by equating the analysis of the dust and the charge to a common basis with copper equal to 100 and the remaining elements adjusted proportionately. The relative elimination of a given element during melting was found by dividing the value for the element in the flue dust by the value for the charge material. The data show that when species in the flue dust are compared to copper, zinc is most readily volatilized, followed by lead, bismuth, tin, antimony, arsenic, copper, and iron.

[5]Keller, Edward. A Study of the Elimination of Impurities From Copper Mattes in the Reverberatory and the Converter. Trans. AIME, v. 28, 1898, pp. 127-159.

TABLE 5. - Partial analyses of flue dust, wt-pct

Element	Test 3	Test 7	Test 11
Antimony	0.14	0.55	0.01
Arsenic	.45	1.40	.64
Bismuth	.07	.08	.06
Copper	2.6	1.9	2.0
Fluorine	22.3	9.9	13.9
Lead	31.7	19.2	30.0
Tin	.13	.42	.03
Zinc	13.5	13.9	12.7

Equipment and Procedures for Engineering-Scale Tests

The 800-kVA electric arc furnace used for the engineering tests is shown in figure 5. Three 4-in-diam graphite electrodes were positioned in a conventional "Delta" configuration on 12-in centers. The cylindrical furnace shell was lined with magnesite bricks, and the furnace hearth was formed of alumina ram mix. The hearth area was 8.3 ft^2, and the maximum depth was approximately 24 in.

The injector system used during several tests is shown on the left in figure 5. The gravimetric feeder shown on the right was used to top-feed the blended charge containing slag, quartz, and pebble lime.

The furnace was equipped with a small baghouse to collect entrained dust from the furnace offgas. The small baghouse and plenum hood were evacuated by a 7,500-cfm fan that exhausted into a positive-pressure cyclone, baghouse, and countercurrent scrubber system.

The proposed technique is based on treating molten converter slags in a separate furnace. This would require another large furnace and crew to remelt the converter slag for each test. Therefore, this investigation was conducted using cold-crushed slag, and the energy data obtained was higher by the amount required to remelt the slag.

During a test, the blended charge containing slag, quartz, and pebble lime was top-fed to the furnace at a rate of 1,000 lb/hr while maintaining a power input of about 250 kW to the furnace. The pyrite-coke breeze mix was added to the furnace through the port on the side and rabbled into the bath at 15-min intervals. During tests utilizing the injection technique patented by Paulson and Hunter,[6] the pyrite-coke breeze mix was injected at about 100 lb/hr, and the slag-quartz-lime charge feed rate was adjusted to introduce the desired stoichiometric amount of sulfur and carbon reductant to the furnace. The progress of the sulfation was monitored by X-ray spectrographic analyses performed on slag samples that were taken every 15 min during the period when pyrite-coke additions were made. The furnace was held at temperature (1,150° to 1,250° C) for 30 min after the completion of feeding to allow for separation of the copper-iron matte and slag. The slag was tapped from the furnace and cooled in conical slag ladles that formed approximately 1,000-lb billets. The copper-iron matte product from the tests was cast into 50-lb pigs. Matte (330-lb) and slag (330-lb) products from previous tests with the same slag were used in the starting nest for subsequent tests to produce conditions representative of a continuous operation.

[6]Paulson, D. L., and W. L. Hunter. Reducing Molten Furnace Slags by Carbon Injection. U.S. Pat. 4,110,107, Aug. 29, 1978.

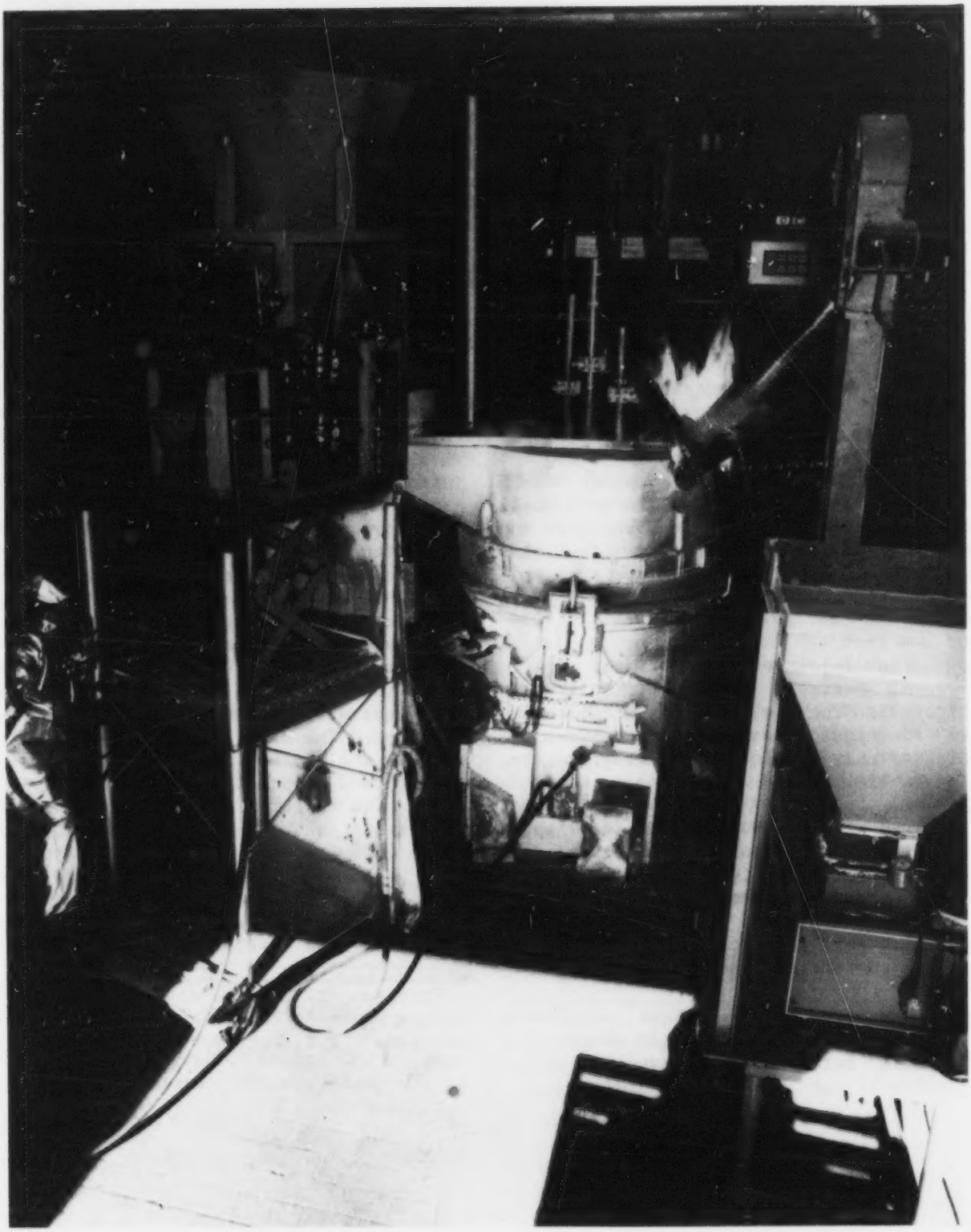

FIGURE 5. - The 800-kVA electric arc furnace and ancillary equipment.

Results of Engineering Tests

Tests were conducted to obtain engineering data on the proposed sulfation technique. Sulfur additions ranged from 29 pct to 113 pct of stoichiometric, based on producing a 40-pct-Cu matte. Data from 15 tests are summarized in tables 6 and 7. Chemical analyses of the matte and slag products are shown in table 8. The range of impurities in the final matte product from each slag source is shown in table 9.

TABLE 6. - Materials distribution for engineering tests

Test	Slag	Charge,[1] lb						Products, lb			Solids recovered, pct
		Slag	Matte	Pebble lime	Quartz	Iron pyrite	Coke breeze	Matte	Slag	Dust	
1....	A	2,345	0	0	126	224	64	263	2,189	16	89
2....	A	2,865	0	0	220	242	52	277	3,015	12	97
3....	A	2,865	0	110	220	242	39	247	2,909	103	93
4....	A	2,622	244	110	242	242	39	448	2,708	39	91
5....	A	2,535	331	165	242	267	42	624	2,663	136	95
6....	B	2,770	0	110	346	154	31	206	3,131	109	100
7....	B	2,657	209	77	276	174	31	364	2,882	66	96
8....	B	1,823	271	50	179	124	26	444	1,950	43	97
9....	B	1,776	318	50	215	78	26	367	1,962	84	97
10....	B	1,763	331	50	215	99	20	328	2,118	86	101
11....	C	2,094	0	86	262	17	54	105	2,364	103	101
12....	C	2,039	55	86	179	26	53	115	2,202	87	97
13....	C	1,929	165	86	179	42	53	171	2,139	79	96
14....	C	1,873	220	86	179	56	53	247	2,100	76	97
15....	C	1,853	241	86	179	26	53	209	2,175	99	101

[1]Iron scrap (29 lb) was used to initiate arc for each test.

The effect of pyrite additions on the recovery of copper from the engineering tests is shown in figure 6. Iron-pyrite additions ranging from 0.40 to 1.56 lb per pound of copper in slag were tested, with the majority of the tests being in the range of 1.01 to 1.56 lb of FeS_2 per pound of copper in the slag. The copper recovery was expected to approach a maximum value, but the scatter in the data made it difficult to determine a value with a reasonable certainty. The copper recovery for slag A increased from 69 pct up to 84 pct over the range of pyrite additions of 1.15 to 1.43 lb per pound of copper in the slag.

These values from the engineering tests were slightly better than those obtained from the laboratory-scale tests, 68 to 73 pct, over the same range of pyrite additions. (See figure 3.) Considerable scatter in the data was obtained for pyrite additions of less than 1.0 lb per pound of copper in the slag and also for slags B and C. The most probable cause for the scatter would be that a percentage of the reductant reacts on the surface of the bath and never gets intimately mixed with the copper in the slag. Slags B and C also have a lower copper content in the slag with which to react. When dealing with slags of lower copper content, such as slag C (2.02 wt-pct Cu), it may be better to make pyrite additions based on a fixed percentage of the weight of slag as described by Barnett.[7]

[7]Barnett, S. C. C. The Methods and Economics of Slag Cleaning. Min. Mag., V. 140, No. 5, May 1979, pp. 408-417.

TABLE 7. - Engineering data from 800-kVA tests

	Slag A					Slag B					Slag C				
	1[1]	2[1]	3[1]	4[1]	5[2]	6[2]	7[2]	8[2]	9[2]	10[1]	11[2]	12[2]	13[2]	14[2]	15[1]
Duration of test.....hr..	4.0	5.2	5.3	4.7	4.4	4.4	4.3	3.2	2.8	2.8	3.1	3.0	3.1	3.0	3.1
Power input.....kW..	196	204	218	210	232	255	260	269	286	336	288	270	272	273	286
Energy consumption kwhr ton^{-1}charge..	590	640	670	560	520	555	555	635	565	700	635	565	600	590	620
Copper sulfidation rate,[3] $lb\text{-}ft^{-2}hr^{-1}$..	4.2	3.8	3.1	7.2	8.8	5.5	9.1	15.6	12.9	13.1	3.2	3.3	4.8	7.3	8.3
Stoichiometric sulfur[4] pct..	94	83	83	91	103	92	108	113	73	93	29	45	78	107	50
Sulfur efficiency[5]...pct..	41	41	32	45	52	44	51	72	57	58	43	40	41	51	46
Slag Cu.....wt-pct..	1.05	1.37	1.07	1.10	0.92	1.07	1.11	1.21	0.99	0.92	1.38	1.12	1.10	1.14	1.16
Matte grade.....wt-pct..	42.2	46.1	41.3	47.7	36.1	61.2	53.5	53.9	47.2	54.7	44.1	41.0	41.8	43.1	60.5
Ratio, Cu in slag/Cu in matte.....	0.025	0.030	0.026	0.023	0.026	0.018	0.021	0.022	0.021	0.017	0.031	0.027	0.026	0.026	0.019
Cu recovery[6].....pct..	84	75	69	81	80	>100	87	73	73	81	73	65	62	77	85

[1]Pyrite-coke breeze injected into molten bath.
[2]Pyrite-coke breeze rabbled into molten bath (15-minute intervals).
[3]Based on surface area of matte--slag interface.
[4]Based on producing a 40 pct Cu matte.
[5]Defined as $\frac{\text{Weight sulfur, matte}}{\text{total sulfur, input}} \times 100$.
[6]Defined as $\frac{\text{Weight copper, matte}}{\text{total copper, input}} \times 100$.

TABLE 8. - Chemical analyses of matte and slag products

Test	Product	Components, wt-pct											
		Cu	Fe	S	Pb	Zn	As	Ni	Mo	CaO	MgO	Al_2O_4	SiO_2
1.....	Matte	42.2	17.9	23.8	7.36	0.53	0.24	NA	NA	NA	NA	NA	NA
	Slag	1.05	43.2	1.40	NA	NA	NA	NA	NA	0.83	1.49	1.59	33.0
2.....	Matte	46.1	15.7	25.3	3.95	.46	.22	NA	NA	NA	NA	NA	NA
	Slag	1.37	41.4	1.34	NA	NA	NA	NA	NA	.77	.85	1.14	35.2
3.....	Matte	41.3	18.0	23.3	6.07	.49	.26	NA	NA	NA	NA	NA	NA
	Slag	1.07	40.2	1.26	NA	NA	NA	NA	NA	3.64	3.27	1.61	35.6
4.....	Matte	47.7	12.9	22.5	7.10	4.84	.26	NA	NA	NA	NA	NA	NA
	Slag	1.10	39.1	1.01	NA	NA	NA	NA	NA	4.04	1.73	.92	34.6
5.....	Matte	36.1	23.9	21.5	6.85	.93	.26	NA	NA	NA	NA	NA	NA
	Slag	.92	39.5	1.29	NA	NA	NA	NA	NA	7.25	1.31	1.34	34.3
6.....	Matte	61.2	9.62	23.1	2.75	1.30	.26	0.65	NA	NA	NA	NA	NA
	Slag	1.07	37.3	NA	.91	6.13	.06	NA	NA	4.86	NA	1.97	34.8
7.....	Matte	53.5	14.6	23.1	2.73	1.28	.22	.61	NA	NA	NA	NA	NA
	Slag	1.11	37.9	NA	NA	NA	NA	NA	NA	4.42	2.51	1.82	36.1
8.....	Matte	53.9	16.8	23.4	2.87	1.42	.29	.69	NA	NA	NA	NA	NA
	Slag	1.21	35.9	.93	NA	NA	NA	NA	NA	4.42	4.51	2.00	34.0
9.....	Matte	47.2	17.4	20.4	2.31	1.37	.26	.58	NA	NA	NA	NA	NA
	Slag	.99	36.5	.77	NA	NA	NA	NA	NA	5.38	2.98	1.94	36.8
10.....	Matte	54.7	13.3	24.1	2.25	1.29	.18	.76	NA	NA	NA	NA	NA
	Slag	.92	33.7	.79	.49	3.23	.02	.04	NA	5.19	7.04	2.17	34.0
11.....	Matte	44.1	28.9	22.6	.45	.94	NA	.34	0.21	NA	NA	NA	NA
	Slag	1.38	40.6	1.12	NA	NA	NA	NA	NA	3.57	3.30	3.18	36.0
12.....	Matte	41.0	33.4	22.8	.25	NA	NA	.16	.09	NA	NA	NA	NA
	Slag	1.12	39.7	1.22	NA	NA	NA	NA	NA	4.81	3.12	2.80	34.7
13.....	Matte	41.8	31.7	23.4	.30	.11	NA	.19	.08	NA	NA	NA	NA
	Slag	1.10	40.7	1.41	NA	NA	NA	NA	NA	4.78	2.68	3.15	33.6
14.....	Matte	43.1	31.0	24.7	4.31	.10	NA	.98	.02	NA	NA	NA	NA
	Slag	1.14	39.9	1.42	NA	NA	NA	NA	NA	4.89	2.71	3.20	34.8
15.....	Matte	60.5	13.0	24.3	.15	.60	.05	.40	<.001	NA	NA	NA	NA
	Slag	1.16	41.6	.94	.04	.54	.02	NA	NA	4.81	3.33	2.86	31.7

NA Not analyzed.

TABLE 9. - Range of impurities in matte product,[1] wt-pct

Element	Slag A	Slag B	Slag C
Aluminum	0.001 - 0.01	ND	0.01 -0.1
Antimony	.03 - .3	0.01 - 0.1	.01 - .1
Arsenic	.1 - 1	.003- .3	.01 - .1
Bismuth	.003 - .03	ND	ND
Chromium	.003 - .03	ND	.01 - .1
Cobalt	.03 - .3	.03 - .3	.03 - .3
Lead	1 -10	.1 - 1	.03 - .3
Magnesium	.0003- .003	.001- .01	.03 - .3
Manganese	.003 - .03	.003- .03	.003- .03
Nickel	.3 - 3	.3 - 3	.1 -1
Silicon	.001 - .01	.01 - .1	.3 -3
Silver	.01 - .1	.001- .01	.001- .01
Tin	.1 - 1	.01 - .1	.01 - .1
Titanium	.001 - .01	ND	ND
Zinc	.1 - 1	1 -10	.03 - .3
Zirconium	.003 - .03	ND	ND

ND Not detected.
[1]Analyzed by qualitative, semiquantitative, X-ray spectroscopy.

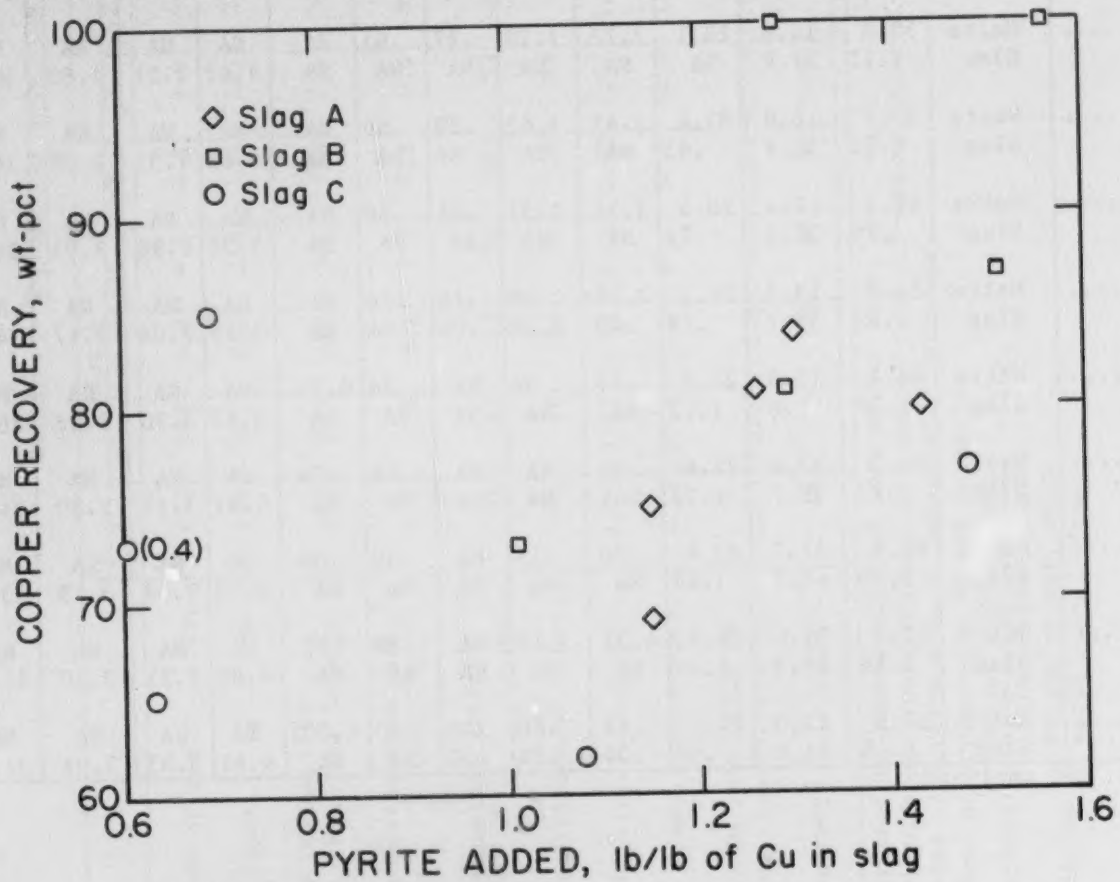

FIGURE 6. - Effect of pyrite on copper recovery, engineering tests.

Pyrite additions greater than 1.56 lb per pound of copper in the slag were not tested during this phase of the investigation. The X-ray spectrographic analyses performed during the tests showed copper contents remaining in the slag to be in the range of 0.3 to 0.5 pct Cu. Therefore, these slags were already reduced in copper content to the level of typically discarded smelting furnace slags. It was later learned that these analyses had been biased by the removal of metal prills prior to the analyses and that the copper content was actually 0.92 to 1.38 wt-pct Cu. However, the range of the biased analyses should be a reasonable endpoint if the slags were allowed to settle for a longer period of time (5 hr).

The results from the 15 tests are also shown in figure 7. The solid lines in the figure show ratios of copper in slag to copper in matte of 0.02 and 0.03, and most of the data from the test series

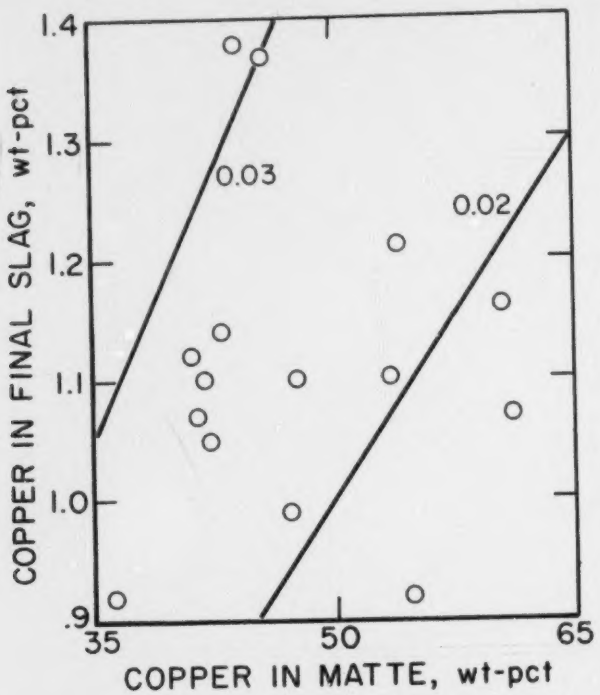

FIGURE 7. - Ratio of copper in slag to copper in matte for engineering tests.

are included in the above range. These values are slightly higher than experimental and industrial studies[8] with matte of industrial grade, 30 to 50 pct Cu, which shows that the ratio is typically 0.01 to 0.02 in industrial operations. If the 0.5-pct-Cu value from the biased analyses is used with the data in table 7, the ratio obtained would be 0.008 to 0.014. The authors believe that increasing the settling time to 5 hr would allow the copper-in-slag concentration to decrease to a value of about 0.5 pct.

A recyclable copper-iron matte (36 to 61 pct Cu) was produced, as a result of this investigation, at an energy consumption of 520 to 700 kwhr per ton of charge. A recent report on industrial operations indicates that industrial slag cleaning furnaces in the range of 5 to 9 MVA typically consume 100 kWh per ton of molten slag treated and 545 kWh per ton of solid material charged.[9] Therefore, the expected energy saving for treating molten slag rather than solid material should be about 400 kWh per ton of slag treated.

This process is comparable, in energy consumption, to the molten slag treatment process, which is being successfully used in both the Outokumpu flash smelting and Mitsubishi processes. Since the converter slag is not returned to the matte smelting furnace, the present process has the additional benefit of eliminating a source of magnetite in the smelting furnace, eliminating the need for additional flux burden to the furnace, and increasing the capacity of the furnace to smelt copper concentrates. The capital and operating costs would have to be calculated on a basis of tons of slag to be treated per year and contained copper, to determine if the process could be economically justified in each individual case.

[8]Pages 80-98 and 204-215 of work cited in footnote 4.

[9]Work cited in footnote 7.

CONCLUSIONS

Treating molten copper converter slags in a separate electric furnace by introducing a sulfur reductant produced a recyclable copper-iron matte. Results of laboratory-scale (50-lb) tests showed that:

1. Increasing the silica content of the slag to saturation (34 to 40 pct) increased the recovery of copper only if the amount of reductant exceeded the stoichiometric requirement.

2. Copper recovery was maximized at about 2.0 to 2.3 lb of pyrite per pound of copper in the slag.

3. Small additions of lime and alumina, which tend to stabilize the slag structure, were detrimental to the recovery of copper from converter slag.

Results of engineering (1-ton) tests on three converter slags containing 2.0 to 7.3 wt-pct Cu showed that:

1. Additions of iron pyrite to provide 29 to 113 pct of the stoichiometric sulfur requirement for a 40-pct-Cu matte produced a recyclable copper-iron matte (36 to 61 pct Cu).

2. The energy required to produce a recyclable copper-iron matte was 520 to 700 kWh per ton of charge.

3. The expected energy saving for treating molten slag should be about 400 kWh per ton of slag treated.

The proposed process is comparable in energy consumption to the commercially successful process used with the Outokumpu flash smelting and Mitsubishi processes, but capital and operation costs would have to be calculated for each individual case to determine if it would be economically justified.

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